



D E C L A R A T I O N

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I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made, are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this *6th* day of September 1999

Shinichi Usui

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6-39389

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[Title of Invention]

PROCESS FOR PRODUCTION OF SEMICONDUCTOR SUBSTRATE

[Scope of Claim]

1. A process for producing a semiconductor substrate, characterized by the steps of making porous a surface layer of at least a main face side of a first Si substrate; forming a monocrystalline semiconductor layer on the porous Si layer of the first substrate; bonding the monocrystalline semiconductor layer to a main face of a supporting substrate separately prepared; separating a resulting bonded substrate at the porous layer; and removing selectively only the porous Si layer exposed on the surface of the face of the supporting substrate produced by the removing.

2. A process for producing a semiconductor substrate, characterized by the steps of making porous surface layers of both sides of a first Si substrate, forming a monocrystalline semiconductor layer on each of the porous Si layers on the both faces; bonding each of main faces of two separately prepared supporting substrates onto the respective

monocrystalline semiconductor layers formed on the both faces of the first Si substrate;
separating the bonded wafer into three at the two porous Si layers; and
removing selectively only the porous Si layers exposed on the surfaces of the separated two supporting substrate sides.

3. The process for producing a semiconductor substrate according to claim 1 or 2, wherein the monocrystalline semiconductor layer of the first Si substrate and the supporting substrate are bonded with interposition of an insulative layer.

4. The process for producing a semiconductor substrate according to claim 1, 2, or 3, wherein the porous Si remaining on the first Si substrate after the separation is removed, and the first Si substrate is reused.

5. The process for producing a semiconductor substrate according to any of claims 1 to 4, wherein the monocrystalline semiconductor layer is a monocrystalline Si layer.

6. The process for producing a semiconductor according to any of claims 1 to 4, wherein the monocrystalline semiconductor layer is a monocrystalline compound semiconductor layer.

7. The process for producing a semiconductor substrate according to any of claims 1 to 4, the

supporting substrate is a Si substrate.

8. The process for producing a semiconductor substrate according to claim any of claims 1 to 4, wherein the supporting substrate is a light-transmissive substrate.

9. The process for producing a semiconductor substrate according to any of claims 2, 3, and 4, wherein the two supporting substrates are selected independently from Si substrates and light-transmissive substrates.

10. The process for producing a semiconductor substrate according to any of claims 1 to 4, wherein the porous Si layer is removed selectively by nonelectrolytic wet chemical etching by immersion in hydrofluoric acid, a mixture solution of hydrofluoric acid and at least one of an alcohol and an aqueous hydrogen peroxide, buffered hydrofluoric acid, or a mixture solution of buffered hydrofluoric acid and at least one of an alcohol and an aqueous hydrogen peroxide.

11. The process for producing a semiconductor substrate according to claim 6, wherein the porous Si layer is removed selectively by chemical etching of only the porous Si by use of an etching solution which etches the porous Si at a higher rate than the compound semiconductor.

12. The process for producing a semiconductor

substrate according to claim 1, 2, or 3, wherein the porous Si layer is removed by selective grinding of the porous Si layer by utilizing the monocrystalline layer as a stopper.

13. The process for producing a semiconductor substrate according to any of claims 1 to 4, wherein the step of separating the bonded substrates at the porous layer is conducted at least by one of the methods of application of a compression force to the substrate in a direction perpendicular to a face of the substrate parallel to the bonding face of the bonded wafer, application of a pulling force to the substrate in a direction perpendicular to the bonding face of the substrate, and application of a shear stress to the bonding face.

14. The process for producing a semiconductor substrate according to claim 3, wherein the insulative layer is formed on at least one of the monocrystalline layer and the main face of the supporting Si substrate.

15. The process for producing a semiconductor substrate according to claim 14, wherein the insulative layer is selected from thermal oxidation films, deposited SiO_2 films, deposited Si_3N_4 films, and multiple layer films thereof.

16. The process for producing a semiconductor substrate according to claim 3, which process an insulative thin plate is used as the insulative layer

in, and which process further comprises superposing and bonding it.

17. The process according to claim 1 or 2, wherein the step of bonding is conducted by a method selected from anode coupling, compression, heat-treatment, and combination thereof.

18. The process for producing a semiconductor substrate according to claim 1, 2, or 3, wherein the porous layer is formed by anodization.

19. The process for producing a semiconductor substrate according to claim 18, wherein the anodization is conducted in a HF solution.

20. The process for producing a semiconductor substrate according to any of claims 1 to 4, wherein the step of separating the substrates at the porous layer is conducted by application of a wave energy.

21. The process for producing a semiconductor substrate according to any of claims 1 to 4, wherein the step of separating the substrates at the porous layer is conducted by inserting a separation member from an edge face of the porous layer therein.

22. The process for producing a semiconductor substrate according to any of claims 1 to 4, wherein the step of separating the substrates at the porous layer is conducted by expansion energy of a material impregnated into the porous layer.

23. The process for producing a semiconductor

substrate according to any of claims 1 to 4, wherein the step of separating the substrates at the porous layer is conducted by selective etching of the porous layer at the edge face of the wafer.

[Detailed Description of Invention]

[0001]

[Industrial Application Fields]

The present invention relates to a process for producing a semiconductor substrate. More specifically, the present invention relates to a process for producing a monocrystalline semiconductor on a dielectric-isolated or insulative material, or producing a monocrystalline compound semiconductor on a Si substrate. Further the present invention relates to a process for producing a semiconductor substrate suitable for an electronic device or an integrated circuit formed on a single crystalline semiconductor layer.

[0002]

[Prior Art]

The technique of formation of a monocrystalline Si semiconductor layer on an insulative material is well known as silicon-on-insulator (SOI) technique. The devices prepared by SOI technique have been studied comprehensively, since it has various advantages which are not achievable by a bulk Si substrate of usual Si

integrated circuits. The SOI technique as advantages as below:

1. Ease of dielectric isolation, and possibility of high degree of integration,
2. High resistance against radioactive ray,
3. Low floating capacity, and possibility of high speed operation,
4. Needlessness of the welling process,
5. Preventability of latch-up,
6. Possibility of producing a complete depletion type field-effect transistor by thinning of the film, and so forth.

[0003]

The process of forming the SOI structure has been studied for several decades to realize the above many advantages in the device properties. The results of the studies are summarized, for example, in the literature below:

[0004]

Special Issue; "Single-crystal silicon on non-single-crystal insulators"; edited by G.W. Cullen, Journal of Crystal Growth; Vol.63, No.3, pp.429-590 (1983).

Further, SOS (silicon on sapphire) is known which is formed by heteroepitaxial growth of silicon on a monocrystalline sapphire substrate by CVD (chemical vapor deposition). The SOS technique, which was successful as one of the SOI techniques, is limited in

the application fields, because of many crystal defects caused by mismatch of the lattice at the interface between the Si layer and the underlying sapphire substrate, contamination of the Si layer with aluminum from the sapphire substrate, and above all, expensiveness of the substrate, and difficulty of large-area substrate formation. Relatively recently, studies are being made to produce the SOI structure without using a sapphire substrate. The studied processes are classified roughly into the two processes below:

[0005]

1. A process which includes surface oxidation of a monocrystalline Si substrate, local exposure of the Si substrate by opening a window, and epitaxial growth of Si laterally from the exposed portion as the seed to form a Si layer on SiO_2 . (Si layer deposition on SiO_2)
2. A process which includes SiO_2 formation at the bottom portion of a monocrystalline Si substrate, utilizing the Si substrate as the active layer. (No Si layer deposition)

The device formed on a compound semiconductor exhibits high performances, such as high speed, and luminescence, which are not achievable by Si. At present, such types of devices are formed by epitaxial growth on a compound semiconductor substrate such as GaAs.

[0006]

The compound semiconductor substrate, however, has disadvantages of high cost, low mechanical strength, and difficulty in formation of a large-area wafer.

[0007]

Accordingly, heteroepitaxial growth of a compound semiconductor on a Si wafer is being studied to attain low cost, high mechanical strength, and ease of production of a large-area wafer.

[0008]

[Problems to Be Solved by Invention]

The above known process 1 includes methods of direct lateral epitaxial growth of a monocrystalline Si layer by CVD; deposition of amorphous Si and subsequent heat treatment to cause solid-phase lateral epitaxial growth; melting recrystallization to grow monocrystalline layer on a SiO_2 by irradiation of amorphous or polycrystalline Si layer with a focused energy beam such as an electron beam and a laser beam; and zone melting recrystallization in which a bar-shaped heater is moved to scan with a belt-like melt zone. These methods respectively have advantages and disadvantages, involving problems in process controllability, productivity, product uniformity, and product quality, and are not industrialized yet. For example, the CVD method requires sacrificial oxidation,

resulting in low crystallinity in the solid-phase growth. The beam annealing method involves problems in processing time of focused beam scanning and in controllability of beam superposition and focusing. Of the above methods, the zone melting recrystallization is the most advanced method, and is employed in relatively large-scale integrated circuits. This method, however, still causes crystal defects in sub-grain boundaries, and is not successful in the production of a minority carrier device.

[0009]

The above known process 2 in which the Si substrate is not utilized as the seed for epitaxial growth includes the four methods below:

[0010]

1. An oxidation film is formed on a monocrystalline Si substrate which has V-shaped grooves on the surface formed by anisotropical etching; a polycrystalline Si layer is deposited in a thickness approximate to that of the Si substrate on the oxidation film; and the back face of the Si substrate is ground to form a monocrystalline Si region isolated dielectrically by surrounding with the V-shaped grooves. This method involves problems in controllability and productivity in deposition of polycrystalline Si in a thickness of as large as several hundred microns, and in removal of the

monocrystalline Si substrate by grinding at the back face to leave an isolated active Si layer only, although the crystallinity is satisfactory.

[0011]

2. A SiO_2 layer is formed by ion implantation into a monocrystalline Si substrate (SIMOX: separation by ion implanted oxygen). This is the most highly advanced method in view of the matching with the Si process. This method, however, requires implantation of oxygen ions in an amount of as much as 10^{15} ions/ cm^2 or more, which takes a long time, resulting in low productivity and high wafer cost. Further, the product has many remaining crystal defects, and does not have the satisfactory quality for the industrial production of a minority carrier device.

[0012]

3. An SOI structure is formed by oxidation of porous Si for dielectric isolation. In this method, an N-type Si layer is formed in an island-like pattern on a P-type monocrystalline Si substrate surface by proton ion implantation (Imai, et al.: J. Crystal Growth, Vol. 63, 547 (1983)) or by epitaxial growth and patterning, and subsequently only the P-type Si substrate is made porous by anodic oxidation in a HF solution to surround the island-patterned N-type Si, and the N-type Si island is dielectrically isolated by accelerated oxidation. In this method, the isolated Si regions are

decided prior to the device process, which may limit the freedom in device design disadvantageously.

[0013]

Being different from the above conventional SOI formation, a method has recently come to be noticed in which a monocrystalline Si substrate is bonded to another thermally oxidized monocrystalline Si substrate by heat treatment or use of an adhesive to form an SOI structure. This method requires uniform thinness of the active layer for the device: namely, formation of a film of a micron thick or thinner from a monocrystalline substrate of several hundred microns thick. This thin film may be formed by either of the two methods below.

[0014]

1. Thin film formation by grinding, and
2. Thin film formation by selective etching.

The grinding method 1 does not readily give a uniform thin film. In particular, formation of a film of submicron thickness results in thickness variation of tens of percent. This irregularity is a serious problem. With a larger diameter of the wafer, the uniformity of the thickness is much more difficult to attain.

[0015]

The etching method 2 is regarded to be effective for uniform thin film formation. This

method, however, involves the problems:

- Insufficient selectivity of about 10^2 at the highest,
- Inferior surface properties after etching, and
- Low crystallinity of the SOI layer because of the employed ion implantation, and epitaxial or heteroepitaxial growth on a high-concentration B-doped Si layer. (C. Harendt, et al.: J. Elect. Mater., Vol. 20, 267 (1991); H. Baumgart, et al.: Extended Abstract of ECS 1st International Symposium of Wafer Bonding, pp.733- (1991); and C.E. Hunt: Extended Abstract of ECS 1st International Symposium of Wafer Bonding, pp.696- (1991))

[0016]

The semiconductor substrate which is prepared by lamination-bonding requires two wafers essentially, and a major part of one of the wafers is discarded by grinding or etching, thereby wasting the resource of the earth.

[0017]

Therefore, the SOI prepared by lamination in conventional processes involves many problems in controllability, uniformity, production cost, and so forth.

[0018]

A thin Si layer deposited on a light-transmissive substrate typified by a glass plate

becomes amorphous or polycrystalline owing to disorder of crystallinity of the substrate, not giving high performance of the device. Simple deposition of Si does not give desired quality of single crystal layer owing to the amorphous crystal structure of the substrate.

[0019]

The light-transmissive substrate is important in construction of a light-receiving element such as a contact sensor, and projection type of liquid crystal image-displaying apparatus. Additionally, a driving element of high performance is necessary for higher density, higher resolution, and higher precision of the sensor and of the image elements of the display. Consequently, the element provided on a light-transmissive substrate is also required to have a monocrystalline layer of high crystallinity.

[0020]

Amorphous Si or polycrystalline Si will not give a driving element having the sufficient performance which is required or will be required, because of the many defects in the crystal structure.

[0021]

As mentioned above, production of a compound semiconductor device requires essentially a compound semiconductor substrate. The compound semiconductor substrate, however, is expensive, and is not readily

formed in a larger size.

[0022]

Epitaxial growth of a compound semiconductor such as GaAs on a Si substrate is investigated. However, it gives a grown film of poor crystallinity owing to the differences in the lattice constants and the thermal expansion coefficients, thereby the resulting grown film being unsuitable for use for a device.

[0023]

Epitaxial growth of a compound semiconductor on porous Si is intended for mitigation of misfit of the lattices. However, the substrate does not have sufficient stability and reliability owing to the low thermal stability and long-term deterioration of the porous Si.

[0024]

An object of the present invention is to obtain a semiconductor layer of a compound semiconductor layer with few defects on an insulative material by preparing a monocrystalline substrate which is economically excellent and uniformly flat over a large area and has an exceedingly excellent crystallinity, and removing a portion thereof from one face of the substrate reaching to an active compound semiconductor layer while leaving a Si layer or the active compound semiconductor layer formed on a surface thereof.

[0025]

Another object of the present invention is to provide a process for producing a semiconductor substrate in which a monocrystalline Si or compound semiconductor layer having crystallinity as high as that of a monocrystalline wafer is formed on a transparent substrate (light-transmissive substrate) with high productivity, high uniformity, high controllability, and low production cost.

[0026]

Still another object of the present invention is to provide a process for producing a semiconductor substrate useful in place of expensive SOS or SIMOX in also the production of a large scale integrated circuit of SOI structure.

[0027]

[Means for Solving Problems]

As the means for solving the aforementioned problems, a first embodiment of the process for producing a semiconductor substrate of the present invention is characterized in that the process comprises the steps of making porous a surface layer of at least a main face side of a first Si substrate, forming a monocrystalline Si layer on the porous Si layer, bonding the monocrystalline Si layer onto a main face of a separately prepared second substrate with interposition of an insulative layer, separating the

bonded substrates at the porous layer, and removing selectively only the porous layer exposed on the surface of the second Si substrate.

[0028]

Another embodiment of the process for producing a semiconductor substrate of the present invention is characterized in that the process comprises the steps of making porous a surface layer of at least a main face side of a first Si substrate, forming a monocrystalline Si layer on the porous Si layer, bonding the monocrystalline Si layer to a main face of a separately prepared light-transmissive substrate with or without interposition of an insulative layer, separating the bonded wafer at the porous layer, and removing selectively only the porous Si layer exposed on the surface of the light-transmissive substrate side.

[0029]

Still another embodiment of the process for producing a semiconductor substrate of the present invention is characterized in that the process comprises the steps of making porous a surface layer of at least a main face side of a first Si substrate, forming a monocrystalline compound semiconductor layer on the porous Si layer, bonding the monocrystalline compound semiconductor layer onto a main face of a second Si substrate different from the first Si

substrate with or without interposition of an insulative layer, separating the bonded wafer at the porous layer, and removing selectively only the porous Si layer exposed on the surface of the second Si substrate side.

[0030]

A further embodiment of the process for producing a semiconductor substrate of the present invention is characterized in that the process comprises the steps of making porous a surface layer of at least a main face side of a first Si substrate, forming a monocrystalline compound semiconductor layer on the porous Si layer, bonding the monocrystalline compound semiconductor layer onto a main face of a separately prepared light-transmissive substrate with or without interposition of an insulative layer, separating the bonded wafer at the porous layer, and removing selectively only the porous Si layer bared on the surface of the light-transmissive substrate side.

[0031]

[Effects]

According to the present invention, the first Si substrate can be removed over a large area at the porous layer. The separated first substrate can be reused as the first Si substrate after the remaining porous layer is removed, and after the surface is treated for surface-flattening treatment if the surface

flatness is insufficient. The first Si substrate can be reused repeatedly so far as it has necessary strength for the use.

[0032]

Further, according to the process for producing a semiconductor substrate of the present invention, two semiconductor substrates can be produced simultaneously by forming a porous Si layer and a nonporous monocrystalline layer on each of the both faces of a first substrate, bonding thereto two supporting substrates, and separating the substrates at the porous layer.

[0033]

The mechanical strength of porous silicon is much lower than that of bulk silicon depending on the porosity thereof. For instance, porous silicon having a porosity of 50% is considered to have half the mechanical strength of bulk silicon. Therefore, on application of a compressive force, a tensile force, or a shearing force to a laminated wafer, the porous layer will be broken first. The larger the porosity of the porous layer is, the less the force for the breakdown of the layer is.

[0034]

In production of a bonded substrate by a prior art technique, the portions of the first Si substrate are successively removed from one face by grinding or

etching, so that both of the faces of the substrate can not be used effectively for a bonding of the supporting substrate. However, according to the present invention, the first substrate is retained unchanged except the surface layer. Therefore, two bonded substrates can be produced simultaneously by use of one first Si substrate by bonding a supporting substrate to each of both main faces of the first Si substrate. Naturally in this case also, the first Si substrate can be reused as the first Si substrate after removal of the remaining porous layers and grinding of the surfaces.

[0035]

Further, according to the process for producing a semiconductor substrate of the present invention, monocrystalline Si or a monocrystalline compound semiconductor having excellent crystallinity and uniform flatness over the large area can be produced by selective etching with remarkable selectivity.

[0036]

Furthermore, according to the present invention, the porous Si layer can be removed by selective grinding by utilizing the monocrystalline layer as the grinding-stopper owing to the low mechanical strength and large surface area of the porous Si.

[0037]

Further, according to the present invention, a monocrystalline compound semiconductor layer can be formed with high crystallinity on porous Si, and this semiconductor layer can be transferred onto an inexpensive insulative substrate of a large area. Thereby, a compound semiconductor layer can be formed with high crystallinity on an insulative substrate with sufficient control of the differences in the lattice constants and in the thermal expansion coefficients which are the problems mentioned above.

[0038]

A silicon substrate can be made porous by anodization in a HF solution. The resulting porous Si layer has a density ranging from 1.1 to 0.6 g/cm³ depending on the HF solution concentration ranging from 50% to 20% in comparison with the density of 2.33 g/cm³ of monocrystalline Si. The porous layer is formed only on a P-type Si substrate, but is not formed on an N-type Si layer for the reasons described later. The porous Si layer has pores of about 600 Å in average diameter according to transmissive electron microscopy.

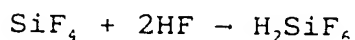
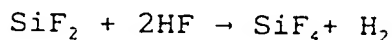
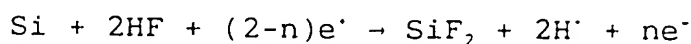
[0039]

The porous Si was found by Uhler, et al. in the year 1956 during the study of electropolishing of semiconductors (A. Uhler: Bell Syst. Tech. J., vol. 35, 333 (1956)).

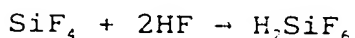
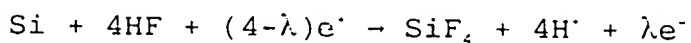
[0040]

Unagami, et al. studied Si dissolution reaction in anodization, and found that positive holes are required for anodization of Si in a HF solution, and the reactions proceed as shown below (T. Unagami, et al.: J. Electrochem. Soc., vol. 127, 476 (1980)).

[0041]



or



where e^+ and e^- represent respectively a positive hole and an electron; n and λ represent respectively the number of positive holes required for dissolving one Si atom. Unagami reported that porous Si is formed under the condition of $n > 2$, or $\lambda > 4$.

[0042]

According to the above consideration, P-type Si which has positive holes can be made porous, whereas N-type Si cannot be made porous. This selectivity for porosity was evidenced by Nagano, et al., and Imai (Nagano, Nakajima, Yasuno, Oonaka, and Kajihara: Denshi Tsushin Gakkai Gijutsu Kenkyu Hokoku (Technical Research Report of Electronic Communication Society) vol. 79, SSD79-9549 (1979); and K. Imai: Solid-State Electronics, vol. 24, p. 159 (1981)).

[0043]

On the other hand, a report is found that high concentration N-type Si can be made porous (R.P. Holmstrom and J.Y. Chi: Appl. Phys. Lett., vol. 42, p. 386 (1983)). Therefore, selection of the substrate is important for producing porous Si regardless of P-type or N-type.

[0044]

The porous Si layer has pores of about 600 Å in average diameter by observation by transmission electron microscopy, and the density is less than half that of monocrystalline Si. Nevertheless, the single crystallinity is maintained, and thereon a monocrystalline Si can be made to grow epitaxially in a layer. However, in the epitaxial growth at a temperature of 1000°C or higher, the internal pores will come to be rearranged, which impairs the accelerated etching characteristics. Therefore, low temperature growth processes are preferred for epitaxial growth of the Si layer, such as molecular beam epitaxial growth, plasma CVD, reduced pressure CVD, photo-assisted CVD, bias sputtering, and liquid-phase epitaxial growth.

[0045]

The porous layer has a large volume of voids therein to have a density reduced by half or lower, and to have a surface area remarkably large for the volume.

Accordingly, the chemical etching is greatly accelerated in comparison with that of the normal monocrystalline layer.

[0046]

[Embodiment 1]

A first monocrystalline Si substrate 11 is made porous at the surface to form a porous layer 12 as shown in Fig. 1(a). Then, the monocrystalline Si layer 13 is formed on the porous Si layer 12 (Fig. 1(b)).

[0047]

Another Si supporting substrate 14 is brought into close contact with the monocrystalline Si layer 13 with interposition of an insulative layer 15 at room temperature as shown in Fig. 1(c), and then the contacted matter was subjected to anode coupling, compression, heat treatment, or combination thereof to bond tightly the Si supporting substrate 14 and the monocrystalline layer 13 with interposition of the insulative layer 15. The insulative layer 15 may be formed preliminarily on at least one of the monocrystalline Si layer and the Si supporting substrate 14, or the three sheets may be bonded with the insulative thin film placed inside.

[0048]

Subsequently, the substrates are separated at the porous Si layer 12 (Fig. 1(d)). On the Si supporting substrate side, the layers have the

structure of porous Si 12 / monocrystalline Si layer 13 / insulative layer 15 / Si supporting substrate 14.

[0049]

The porous Si 12 is removed selectively by non-electrolytic wet chemical etching by use of at least one of a usual Si etching solution, hydrofluoric acid as the porous Si-selective etching solution, a mixture of hydrofluoric acid with an alcohol and/or aqueous hydrogen peroxide, and buffered hydrofluoric acid or a mixture of buffered hydrofluoric acid with alcohol and/or aqueous hydrogen peroxide to leave the thin-layered monocrystalline Si layer 13 on the insulative substrate 15+14. As described above in detail, the porous Si can be etched selectively by a usual Si etching solution owing to the extremely large surface area of the porous surface area.

[0050]

Otherwise, the porous Si 12 is selectively removed by grinding by utilizing the monocrystalline Si layer 13 as the grinding stopper.

[0051]

Fig. 1(e) illustrates a semiconductor substrate of the present invention. The monocrystalline Si layer 13 is formed flat and uniformly in a thin layer on the insulative substrate 15+14 over the entire large area of the wafer. The resulting semiconductor substrate is useful for production of insulation-isolated electronic

elements.

[0052]

The first monocrystalline Si substrate 11 can be repeatedly used for the same use after removal of the remaining porous Si, and after surface-flattening treatment if the surface has become roughened unacceptably, in the next production cycle.

[0058]

[Embodiment 2]

A first monocrystalline Si substrate 21 is made porous at the surface to form a porous layer 22 as shown in Fig. 2(a). Then a monocrystalline Si layer 23 is formed on the porous Si layer 22 (Fig. 2(b)).

[0054]

A light-transmissive supporting substrate 24 made of quartz, glass, or the like is brought into close contact with the monocrystalline Si layer 23 with interposition of an insulative layer 25 at room temperature as shown in Fig. 2(c), and then the contacted matter was subjected to anode coupling, compression, heat treatment, or combination thereof to bond tightly the light-transmissive supporting substrate 24 and the monocrystalline layer 23 with interposition of the insulative layer 25. The insulative layer 25 may be formed preliminarily on at least one of the monocrystalline Si layer or the light-transmissive supporting substrate 24, or the three

sheets may be lamination-bonded with the insulative thin film placed inside.

[0055]

Subsequently, the substrates are separated at the porous Si layer 23 (Fig. 2(d)). On the light-transmissive supporting substrate side, the layers have the structure of porous Si 22 / monocrystalline Si layer 23 / insulative layer 25 / light-transmissive supporting substrate 24.

[0056]

The porous Si 22 is removed selectively by non-electrolytic wet chemical etching by use of at least one of a usual Si etching solution, hydrofluoric acid as the porous Si-selective etching solution, a mixture of hydrofluoric acid with an alcohol and/or aqueous hydrogen peroxide, buffered hydrofluoric acid, and a mixture of hydrofluoric acid with an alcohol and/or aqueous hydrogen peroxide to leave a thin-layered monocrystalline Si layer 23 on the insulative substrate 25+24. As described above in detail, the porous Si can be etched selectively by a usual Si etching solution because of the extremely large surface area of the porous Si.

[0057]

Otherwise, the porous Si layer 22 is selectively removed by grinding by utilizing the monocrystalline Si layer 23 as the grinding stopper.

[0058]

Fig. 2(e) illustrates a semiconductor substrate of the present invention. The monocrystalline Si layer 23 is formed flat and uniformly in a thin layer on the light-transmissive insulative substrate 25+24 over the entire large area of the wafer. The obtained semiconductor substrate is useful for production of insulation-isolated electronic elements.

[0059]

The presence of the interposed insulative layer 25 is not essential.

[0060]

The first monocrystalline Si substrate 21 can be repeatedly used for the same use after removal of the remaining porous Si, and after surface-flattening treatment if the surface has become roughened unacceptably, in the next production cycle.

[0061]

[Embodiment 3]

A first monocrystalline Si substrate 31 is made porous at the surface to form a porous layer 32 as shown in Fig. 3(a). Then, a monocrystalline compound semiconductor layer 33 is formed on the porous Si layer 32 (Fig. 3(b)).

[0062]

Another Si supporting substrate 34 is brought into close contact with the monocrystalline compound

semiconductor layer 33 with interposition of an insulative layer 35 at room temperature as shown in Fig. 3(c), and then the contacted matter was subjected to anode coupling, compression, heat treatment, or combination thereof to bond tightly the Si supporting substrate 34 and the monocrystalline layer 33 with interposition of the insulative layer 35. The insulative layer 35 may be formed on at least one of the monocrystalline compound semiconductor layer and the Si supporting substrate 34, or the three sheets may be bonded with the insulative thin film placed therein.

[0063]

Subsequently, the substrates are separated at the porous Si layer 32 (Fig. 3(d)). On the Si supporting substrate side, the layers have the structure of porous Si 32 / monocrystalline compound semiconductor layer 33 / insulative layer 35 / Si supporting substrate 34.

[0064]

The porous Si 32 is removed selectively by chemical etching by use of an etching solution which is capable of etching Si at a higher etching rate than the compound semiconductor to leave the thin-layered monocrystalline compound semiconductor layer 33 on the insulative substrate 35+34.

[0065]

Otherwise, the porous Si 32 is selectively

removed by grinding by utilizing the monocrystalline compound semiconductor layer 33 as the grinding stopper.

[0066]

Fig. 3(e) illustrates a semiconductor substrate of the present invention. The monocrystalline compound semiconductor layer 33 is formed flat and uniformly in a thin layer on the insulative substrate 35+34 over the entire large area of the wafer. The obtained semiconductor substrate is useful as a compound semiconductor substrate, and for production of insulation-isolated electronic elements.

[0067]

When the substrate is used as a compound semiconductor substrate, the insulative layer 35 is not essential.

[0068]

The first monocrystalline Si substrate 31 can be repeatedly used for the same use after removal of the remaining porous Si, and after surface-flattening treatment if the surface has become roughened unacceptably, in the next production cycle.

[0069]

[Embodiment 4]

A first monocrystalline Si substrate 41 is made porous at the surface to form a porous layer 42 as shown in Fig. 4(a). Then a monocrystalline compound

semiconductor layer 43 is formed on the porous Si layer 42 (Fig. 4(b)).

[0070]

A light-transmissive supporting substrate 44 made of quartz, glass, or the like is brought into close contact with the monocrystalline compound semiconductor layer 43 with interposition of an insulative layer 45 at room temperature as shown in Fig. 4(c), and then the contacted matter was subjected to anode coupling, compression, heat treatment, or combination thereof to bond tightly the light-transmissive supporting substrate 44 and the monocrystalline layer 43 with interposition of the insulative layer 45. The insulative layer 45 may be formed preliminarily on at least one of the monocrystalline compound semiconductor layer and the light-transmissive supporting substrate 44, or the three sheets may be bonded with the insulative thin film placed inside.

[0071]

Subsequently, the substrates are separated at the porous Si layer 43 (Fig. 4(d)). On the light-transmissive supporting substrate side, the layers have the structure of porous Si 42 / monocrystalline compound semiconductor layer 43 / insulative layer 45 / light-transmissive supporting substrate 44.

[0072]

The porous Si 42 is removed selectively. The porous Si 42 only is etched by chemical etching by use of an etching solution which is capable of etching Si at a higher etching rate than that of the compound semiconductor to leave a thin-layered monocrystalline compound semiconductor layer 43 on the insulative substrate 45+44.

[0073]

Otherwise, the porous Si 42 is selectively removed by grinding by utilizing the monocrystalline compound semiconductor layer 43 as the grinding stopper.

[0074]

Fig. 4(e) illustrates a semiconductor substrate of the present invention. The monocrystalline compound semiconductor layer 43 is formed flat and uniformly in a thin layer on the insulative substrate 45+44 over the entire large area of the wafer. The obtained semiconductor substrate is useful for production of insulation-isolated electronic elements.

[0075]

The insulative layer 45 is not essential.

[0076]

The first monocrystalline Si substrate 41 can be repeatedly used for the same use after removal of the remaining porous Si, and after surface-flattening treatment if the surface has become roughened

unacceptably, in the next production cycle.

[0077]

[Embodiment 5]

A first monocrystalline Si substrate 51 is made porous at the both faces to form porous layers 52,53 as shown in Fig. 5(a). Then, monocrystalline semiconductor layers 54,55 are formed on the porous Si layers 52,53 (Fig. 5(b)).

[0078]

Two supporting substrates 56,57 are brought into close contact with the monocrystalline semiconductor layers 54,55 with interposition of insulative layers 58,59 respectively at room temperature as shown in Fig. 5(c), and then the contacted matter is subjected to anode coupling, compression, heat treatment, or combination thereof to bond tightly the supporting substrates 56,57 and the monocrystalline layers 54,55 with interposition of the insulative layers 58,59. In the bonding, the respective insulative layers 58,59 may be formed preliminarily on at least one of the monocrystalline semiconductor layers 54,55 or the supporting substrates 56,57 or the five sheets may be bonded with the insulative thin films placed inside.

[0079]

Subsequently, the substrates are separated into three sheets at both porous Si layers 52,53 (Fig.

5(d)). The two supporting substrates come to have a structure of porous Si / monocrystalline semiconductor layer / insulative layer / supporting substrate (52/54/58/56, and 53/55/59/57).

[0080]

The porous Si layers 52,53 are removed selectively by chemical etching to leave thin-layered monocrystalline semiconductor layers 54,55 on the supporting substrates 58/56 and 59/57.

[0081]

Otherwise, the porous Si 52,53 are removed by selective grinding by utilizing the monocrystalline semiconductor layers 54,55 as the grinding stopper.

[0082]

Fig. 5(e) illustrates semiconductor substrates prepared according to the present invention. The monocrystalline compound semiconductor layers are formed flat and uniformly in a thin layer on the supporting substrates over the entire large area of the two wafers at a time. The obtained semiconductor substrate is useful for production of insulation-isolated electronic elements.

[0083]

The insulative intervening layers 58,59 are not essential.

[0084]

The supporting substrates 56,57 need not be the

same.

[0085]

The first monocrystalline Si substrate 51 can be repeatedly used for the same use after removal of the remaining porous Si, and after surface-flattening treatment if the surface has become roughened unacceptably, in the next production cycle.

[0086]

[Examples]

(Example 1)

A first monocrystalline (100) Si substrate of a P-type or N-type having a diameter of 6 inches, a thickness of 625 μm , and a specific resistance of 0.01 $\Omega\cdot\text{cm}$ was anodized in a HF solution.

[0087]

The anodization conditions are shown below:

[0088]

Current density:	5 ($\text{mA}\cdot\text{cm}^{-2}$)
Anodization solution:	HF:H ₂ O:C ₂ H ₅ OH = 1:1:1
Time:	12 (minutes)
Thickness of porous Si:	10 (μm)
Porosity:	15 (%)

This substrate was oxidized at 400°C in an oxygen atmosphere for one hour. By this oxidation, the inner wall of the pores of the porous Si was covered with a thermal oxidation film. On the porous Si, monocrystalline Si was allowed to grow epitaxially in a

thickness of 1 μm by CVD (chemical vapor deposition) under the growth conditions below:

[0089]

Source gas: $\text{SiH}_2\text{Cl}_2/\text{H}_2$
Gas flow rate: 0.5/180 ℓ/min
Gas pressure: 80 Torr
Temperature: 950°C
Growth rate: 0.3 $\mu\text{m}/\text{min}$

The face of the epitaxial Si layer was thermally oxidized to form a SiO_2 layer of 100 nm thick.

[0090]

A face of a separately prepared second Si substrate having a SiO_2 layer of 500 nm thick was brought into contact in superposition with the face of the above SiO_2 layer, and the contacted matter was heat-treated at 900°C for 2 hours to bond the substrates tightly.

[0091]

A sufficient pulling force was applied to the inside of faces of the resulting bonded wafer in the direction perpendicular to the wafer face and uniformly the inside of the face to destroy the porous Si layer and to separate the wafer into two sheets to expose porous Si.

[0092]

Then the porous Si layer is etched selectively in a mixture of 49% hydrofluoric acid and aqueous 30%

hydrogen peroxide (1:5) with agitation. The porous Si was etched and removed completely with the monocrystalline Si remaining unetched as an etching stopper.

[0093]

The etching rate of the nonporous monocrystalline Si was extremely low, the selection ratio of the etching rate of the porous Si being 10^5 or higher. Therefore, the decrease in thickness of the nonporous layer by etching was practicably negligible (several tens of angstrom).

[0094]

Consequently, a monocrystalline Si layer was formed in a thickness of 1 μm on a Si oxidation film. The monocrystalline Si layer did not change at all by the selective etching of the porous Si layer.

[0095]

The cross-section of the Si layer was observed by transmission electron microscopy, and it was confirmed that no additional crystal defect was formed in the Si layer and the excellent crystallinity was retained.

[0096]

The same results were obtained without forming the oxidation film on the face of the epitaxial Si layer surface.

(Example 2)

A first monocrystalline (100) Si substrate of a P-type or N-type having a diameter of 4 inches, a thickness of 525 μm , and a specific resistance of 0.01 $\Omega\cdot\text{cm}$ was anodized in a HF solution.

[0097]

The anodization conditions are shown below.

[0098]

Current density:	7 ($\text{mA}\cdot\text{cm}^{-2}$)
Anodization solution:	HF:H ₂ O:C ₂ H ₅ OH = 1:1:1
Time:	12 (minutes)
Thickness of porous Si:	10 (μm)
Porosity:	15 (%)

This substrate was oxidized at 400°C in an oxygen atmosphere for 2 hours. By this oxidation, the inner wall of the pores of the porous Si was covered with a thermal oxidation film. On the porous Si, monocrystalline Si was allowed to grow epitaxially in a thickness of 0.5 μm by MBE (molecular beam epitaxy) under the growth conditions below.

[0099]

Temperature:	700°C
Pressure:	1×10^{-9} Torr
Growth rate:	0.1 nm/sec
Temperature:	950°C
Growth rate:	0.3 $\mu\text{m}/\text{min}$

The face of the epitaxially grown Si layer was thermally oxidized to form a SiO₂ layer of 100 nm thick.

[0100]

A separately prepared fused quartz substrate was brought into close contact in superposition with the face of the SiO_2 layer, and the contacted matter was heat-treated at 400°C for 2 hours for bonding.

[0101]

A sufficient compression force was applied to the inside of the face of the resulting bonded wafer in the direction perpendicular to the face thereof and uniformly the inside of the face. Thereby, the porous Si layer was broken and the wafer was separated into two sheets with the porous Si exposed.

[0102]

The porous Si layers were etched selectively in a mixture of buffered hydrofluoric acid and aqueous 30% hydrogen peroxide (1:5) with agitation. Thereby the porous Si was etched and removed selectively and completely with the monocrystalline Si remaining unetched as an etch-stop material.

[0103]

The etching rate of the nonporous monocrystalline Si was extremely low, the selection ratio of the etching rate of the porous Si being 10^5 or higher. Therefore, thickness decrease of the nonporous layer by etching was practicably negligible (several tens of angstrom).

[0104]

Consequently, a monocrystalline Si layer was formed in a thickness of 0.5 μm on a fused quartz substrate. The monocrystalline Si layer did not change at all by the selective etching of the porous Si layer.

[0105]

The cross-section of the Si layer was observed by transmission electron microscopy, and it was confirmed that no additional crystal defect was formed in the Si layer and the excellent crystallinity was retained.

[0106]

The same results were obtained without forming the oxidation film on the face of the epitaxial Si layer.

[0107]

(Example 3)

A first monocrystalline (100) Si substrate of a P-type or N-type having a diameter of 6 inches, a thickness of 625 μm , and a specific resistance of 0.01 $\Omega\cdot\text{cm}$ was anodized in a HF solution.

[0108]

The anodization conditions were as shown below.

[0109]

Current density:	7 ($\text{mA}\cdot\text{cm}^{-2}$)
Anodization solution:	HF:H ₂ O:C ₂ H ₅ OH = 1:1:1
Time:	12 (minutes)
Thickness of porous Si:	10 (μm)

Porosity: 15 (%)

This substrate was oxidized at 400°C in an oxygen atmosphere for one hour. By this oxidation, the inner wall of the pores of the porous Si was covered with a thermal oxidation film. On the porous Si, monocrystalline GaAs was allowed to grow epitaxially in a thickness of 1 μm by MOCVD (metal organic chemical vapor deposition) under the growth conditions below.

[0110]

Source gas: TMG / AsH_3 / H_2

Gas pressure: 80 Torr

Temperature: 700°C

A separately prepared second Si substrate was brought into contact in superposition with the face of the formed GaAs layer, contacted matter was heat-treated at 900°C for one hour for bonding. By this heat treatment, the substrates were bonded tightly.

[0111]

A sufficient compression force was applied to the inside of the face of the resulting bonded wafer in the direction perpendicular to the face of the wafer and uniformly in the inside of the face. Thereby, the porous Si layer was broken and the wafer was separated into two sheets with the porous Si exposed.

[0112]

Then, the oxidation film on the inner wall of the porous Si layer was removed by hydrofluoric acid,

and the porous Si was etched with a mixture of ethylenediamine, pyrocatechol, and water (ratio of 17 ml : 3 g : 8 ml) at 110°C. Thereby the porous Si was etched selectively and removed completely with the monocrystalline GaAs remaining unetched as an etch-stopping material.

[0113]

The etching rate of the nonporous monocrystalline GaAs was extremely low, so that the decrease of the layer thickness thereof was practically negligible.

[0114]

Consequently, a monocrystalline GaAs layer was formed in a thickness of 1 μ m on a Si substrate. The monocrystalline GaAs layer did not change at all by the selective etching of the porous Si layer.

[0115]

The cross-section of the GaAs layer was observed by transmission electron microscopy, and it was confirmed that no additional crystal defect was formed in the GaAs layer and the excellent crystallinity was retained.

[0116]

GaAs on an insulative film was also prepared by employing a Si substrate having an oxidation film as the supporting substrate.

[0117]

(Example 4)

A first monocrystalline (100) Si substrate of a P-type or N-type having a diameter of 5 inches, a thickness of 625 μm , and a specific resistance of 0.01 $\Omega\cdot\text{cm}$ was anodized in a HF solution.

[0118]

The anodization conditions were as shown below.

[0119]

Current density:	10 ($\text{mA}\cdot\text{cm}^{-2}$)
Anodization solution:	$\text{HF}:\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 1:1:1$
Time:	24 (minutes)
Thickness of porous Si:	20 (μm)
Porosity:	17 (%)

This substrate was oxidized at 400°C in an oxygen atmosphere for 2 hours. By this oxidation, the inner wall of the pores of the porous Si was covered with a thermal oxidation film. On the porous Si, monocrystalline AlGaAs was allowed to grow epitaxially in a thickness of 0.5 μm by MBE (molecular beam epitaxy).

[0120]

A face of a separately prepared low-melting glass substrate was brought into contact in superposition with the face of the above formed AlGaAs layer. The contacted matter was heat-treated at 500°C for 2 hours for bonding. By this heat-treatment, the two substrates were bonded together tightly.

[0121]

A sufficient compression force was applied to the inside of the face of the resulting bonded wafer in the direction perpendicular to the face of the wafer and uniformly in the inside of the face. Thereby, the porous Si layer was broken and the wafer was separated into two sheets with the porous Si exposed.

[0122]

The porous Si was etched with a hydrofluoric acid solution. Thereby, the porous Si was etched selectively and removed completely with the monocrystalline AlGaAs remaining unetched as an etch-stopping material.

[0123]

The etching rate of the nonporous monocrystalline AlGaAs was extremely low, so that the decrease of layer thickness thereof was practically negligible.

[0124]

Consequently, a monocrystalline AlGaAs layer was formed in a thickness of 0.5 μm on a glass substrate. The monocrystalline AlGaAs layer did not change at all by the selective etching of the porous Si layer.

[0125]

The cross-section of the AlGaAs layer was observed by transmission electron microscopy, and it

was confirmed that no additional crystal defect was formed in the AlGaAs layer and the excellent crystallinity was retained.

[0126]

(Example 5)

A first monocrystalline (100) Si substrate of a P-type or N-type having been ground on the both faces and having a diameter of 6 inches, a thickness of 625 μm , and a specific resistance of $0.01 \Omega \cdot \text{cm}$ was anodized on the both faces in a HF solution.

[0127]

The anodization conditions were as shown below.

[0128]

Current density:	5 ($\text{mA} \cdot \text{cm}^{-2}$)
Anodization solution:	$\text{HF}:\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 1:1:1$
Time:	12 × 2 (minutes)
Thickness of porous Si:	10 (μm) respectively
Porosity:	15 (%)

This substrate was oxidized at 400°C in an oxygen atmosphere for one hour. By this oxidation, the inner wall of the pores of the porous Si was covered with a thermal oxidation film. On the porous Si formed on both faces of the substrate, monocrystalline Si was allowed to grow epitaxially in a thickness of 1 μm respectively by CVD (chemical vapor deposition) under the growth conditions below:

[0129]

Source gas: $\text{SiH}_2\text{Cl}_2/\text{H}_2$
Gas flow rate: 0.5/180 l/min
Gas pressure: 80 Torr
Temperature: 950°C
Growth rate: $0.3 \mu\text{m}/\text{min}$

On the faces of the formed epitaxial Si layers, SiO_2 layers were formed by thermal oxidation in a thickness of 100 nm.

[0130]

A face of a separately prepared Si substrate having a 500-nm thick SiO_2 layer was brought into contact in superposition with each of the faces of the above SiO_2 layers respectively, and the contacted matter was heat-treated at 600°C for 2 hours to bond the substrates tightly.

[0131]

A sufficient pulling force was applied to the inside of the resulting bonded wafer in the direction perpendicular to the bonded wafer face and uniformly in the inside of the face. Thereby, the two porous Si layers were both broken to allow the wafer to separate into three sheets with the porous Si exposed.

[0132]

The porous Si layers were etched selectively with a mixture of 49% hydrofluoric acid and aqueous 30% hydrogen peroxide (1:5) with agitation. Thereby the porous Si was etched selectively and removed completely

with the monocrystalline Si remaining unetched as an etch-stopping material.

[0133]

The etching rate of the nonporous monocrystalline Si was extremely low, the selection ratio of the etching rate of the porous Si being 10^5 or higher. Therefore, the decrease in thickness of the nonporous layer by etching was practically negligible (several tens of angstrom).

[0134]

Consequently, a monocrystalline Si layer was formed in a thickness of 1 μm respectively on the two Si oxidation films simultaneously. The monocrystalline Si layers did not change at all by the selective etching of the porous Si layer.

[0135]

The cross-section of the Si layer was observed by transmission electron microscopy, and it was confirmed that no additional crystal defect was formed in the Si layer and the excellent crystallinity was retained.

[0136]

The same results were obtained without forming the oxidation film on the epitaxial Si layer face.

[0137]

(Example 6)

A first monocrystalline (100) Si substrate of a

P-type or N-type having a diameter of 5 inches, a thickness of 625 μm , and a specific resistance of 0.01 $\Omega\cdot\text{cm}$ was anodized in a HF solution.

[0138]

The anodization conditions were as shown below.

[0139]

Current density:	7 ($\text{mA}\cdot\text{cm}^{-2}$)
Anodization solution:	$\text{HF}:\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 1:1:1$
Time:	4 (minutes)
Thickness of porous Si:	3 (μm)
Porosity:	15 (%)

Subsequently,

Current density:	30 ($\text{mA}\cdot\text{cm}^{-2}$)
Anodization solution:	$\text{HF}:\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 1:3:2$
Time:	3 (minutes)
Thickness of porous Si:	10 (μm)
Porosity:	45 (%)

This substrate was oxidized at 400°C in an oxygen atmosphere for one hour. By this oxidation, the inner wall of the pores of the porous Si was covered with a thermal oxidation film. On the porous Si, monocrystalline Si was allowed to grow epitaxially in a thickness of 0.3 μm by CVD under the conditions below.

[0140]

Source gas:	SiH_4
Carrier gas:	H_2
Temperature:	850°C

Pressure: 1×10^{-2} Torr

Growth rate: 3.3 nm/sec

The surface of the formed epitaxial Si layer was thermally oxidized to form a SiO₂ layer in a thickness of 100 nm.

[0141]

A face of a separately prepared second Si substrate having a 500-nm thick SiO₂ layer was brought into contact in superposition with the face of the above formed SiO₂ layer, and the contacted matter was heat-treated at 700°C for 2 hours for bonding.

[0142]

A sufficient pulling force was applied to the the inside of the face of the resulting bonded wafer in the direction perpendicular to the bonded wafer face and uniformly in the inside of the face. Thereby, the porous Si layer was broken to allow the wafer to separate into two sheets with the porous Si exposed.

[0143]

The porous Si layer was etched selectively with an etching solution of HF/HNO₃/CH₃COOH type. Thereby the porous Si was etched selectively and removed completely.

[0144]

The etching rate of the nonporous monocrystalline Si was extremely low, so that the decrease of the thickness of the nonporous layer by

etching was practically negligible.

[0145]

Consequently, a monocrystalline Si layer was formed in a thickness of 1 μm on the Si oxidation film. The monocrystalline Si layers did not change at all by the selective etching of the porous Si layer.

[0146]

The cross-section of the Si layer was observed by transmission electron microscopy, and it was confirmed that no additional crystal defect was formed in the Si layer and the excellent crystallinity was retained.

[0147]

The same results were obtained without forming the oxidation film on the epitaxial Si layer face.

[0148]

(Example 7)

A first monocrystalline (100) Si substrate of a P-type or N-type having a diameter of 6 inches, a thickness of 625 μm , and a specific resistance of 0.01 $\Omega\cdot\text{cm}$ was anodized in a HF solution.

[0149]

The anodization conditions were as shown below.

[0150]

Current density:	5 ($\text{mA}\cdot\text{cm}^{-2}$)
Anodization solution:	$\text{HF}:\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 1:1:1$
Time:	12 (minutes)

Thickness of porous Si: 10 (μm)

Porosity: 15 (%)

This substrate was oxidized at 400°C in an oxygen atmosphere for one hour. Thereby the inner wall of the pores of the porous Si was covered with a thermal oxidation film. On the porous Si, monocrystalline Si was allowed to grow epitaxially in a thickness of 1 μm by CVD under the growth conditions below.

[0151]

Source gas: $\text{SiH}_2\text{Cl}_2/\text{H}_2$

Gas flow rate: 0.5/180 ℓ/min

Gas pressure: 80 Torr

Temperature: 950°C

Growth rate: 0.3 $\mu\text{m}/\text{min}$

The surface of the formed epitaxial Si layer was thermally oxidized to form a SiO_2 layer in a thickness of 100 nm.

[0152]

A face of a separately prepared Si substrate having a 500-nm thick SiO_2 layer was brought into contact in superposition with the face of the above formed SiO_2 layer, and the contacted matter was heat-treated at 900°C for 2 hours for bonding.

[0153]

A sufficient pulling force was applied to the the inside of the faces of the resulting bonded wafer

the direction perpendicular to the faces and uniformly in the inside of the face. Thereby, the porous Si layer was broken to allow the wafer to separate into two sheets with the porous Si exposed.

[0154]

The porous Si layer on the second substrate was ground selectively by utilizing the monocrystalline layer as the stopper. The porous Si was removed completely by the selective grinding.

[0155]

Consequently, a monocrystalline Si layer was formed in a thickness of 1 μm on the Si oxidation film. The monocrystalline Si layers did not change at all by the selective etching of the porous Si layer.

[0156]

The cross-section of the Si layer was observed by transmission electron microscopy, and it was confirmed that no additional crystal defect was formed in the Si layer and the excellent crystallinity was retained.

[0157]

The same results were obtained without forming the oxidation film on the epitaxial Si layer face.
(Example 8)

A first monocrystalline (100) Si substrate of P-type or N-type having a diameter of 6 inches, a thickness of 625 μm , and a specific resistance of 0.01

$\Omega \cdot \text{cm}$ was anodized in a HF solution.

[0158]

The anodization conditions were as shown below.

[0159]

Current density:	5 ($\text{mA} \cdot \text{cm}^{-2}$)
Anodization solution:	$\text{HF}:\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 1:1:1$
Time:	12 (minutes)
Thickness of porous Si:	10 (μm)
Porosity:	15 (%)

This substrate was oxidized at 400°C in an oxygen atmosphere for one hour. By this oxidation, the inner wall of the pores of the porous Si was covered with a thermal oxidation film. On the porous Si, monocrystalline Si was allowed to grow epitaxially in a thickness of $1 \mu\text{m}$ by CVD (chemical vapor deposition) under the conditions below.

[0160]

Source gas:	$\text{SiH}_2\text{Cl}_2/\text{H}_2$
Gas flow rate:	$0.5/180 \text{ l/min}$
Gas pressure:	80 Torr
Temperature:	950°C
Growth rate:	$0.3 \mu\text{m/min}$

The surface of the formed epitaxial Si layer was thermally oxidized to form a SiO_2 layer in a thickness of 100 nm.

[0161]

A face of a separately prepared Si substrate

having a 500-nm thick SiO_2 layer formed thereon was brought into contact in superposition with the face of the above formed SiO_2 layer, and the contacted matter was heat-treated at 900°C for 2 hours for bonding.

[0162]

Then, a wave energy like supersonic energy was applied to the resulting bonded wafer. Thereby, the porous Si layer was broken to allow the wafer to separate into two sheets with the porous Si exposed.

[0163]

The porous Si layer was etched selectively with a mixture of 49% hydrofluoric acid with aqueous 30% hydrogen peroxide (1:5) with agitation. Thereby, the porous Si was etched selectively and removed completely with the monocrystalline Si remaining unetched as an etch-stopping material.

[0164]

The etching rate of the nonporous monocrystalline Si was extremely low, the selection ratio of the etching rate of the porous Si being 10^5 or higher. Therefore, the decrease in thickness of the nonporous layer by etching was practically negligible (several tens of angstrom).

[0165]

Consequently, a monocrystalline Si layer was formed in a thickness of $1\text{ }\mu\text{m}$ on the Si oxidation film. The monocrystalline Si layer did not change at all by

the selective etching of the porous Si layer.

[0166]

The cross-section of the Si layer was observed by transmission electron microscopy, and it was confirmed that no additional crystal defect was formed in the Si layer and the excellent crystallinity was retained.

[0167]

The same results were obtained without forming the oxidation film on the epitaxial Si layer face.

[0168]

The first monocrystalline Si substrate was used repeatedly for the same use after removal of the porous Si remaining thereon.

[0169]

(Example 9)

A first monocrystalline (100) Si substrate of a P-type or N-type having a diameter of 4 inches, a thickness of 525 μm , and a specific resistance of 0.01 $\Omega\cdot\text{cm}$ was anodized in a HF solution.

[0170]

The anodization conditions were as shown below.

[0171]

Current density:	7 ($\text{mA}\cdot\text{cm}^{-2}$)
Anodization solution:	HF:H ₂ O:C ₂ H ₅ OH = 1:1:1
Time:	12 (minutes)
Thickness of porous Si:	10 (μm)

Porosity: 15 (%)

This substrate was oxidized at 400°C in an oxygen atmosphere for 2 hours. By this oxidation, the inner wall of the pores of the porous Si was covered with a thermal oxidation film. On the porous Si, monocrystalline Si was allowed to grow epitaxially in a thickness of 0.5 μm by MBE (molecular beam epitaxy) under the growth conditions below.

[0172]

Temperature: 700°C
Pressure: 1×10^{-9} Torr
Growth rate: 0.1 nm/sec
Temperature: 950°C
Growth rate: 0.3 $\mu\text{m}/\text{min}$

The surface of the epitaxially grown Si layer was thermally oxidized to form a SiO_2 layer of 100 nm thick.

[0173]

A face of a separately prepared fused quartz substrate was brought into contact in superposition with the face of the SiO_2 layer, and the contacted matter was heat-treated at 400°C for 2 hours for bonding.

[0174]

The end of the porous layer was bared at the edge face of the wafer, and the porous Si is slightly etched. Thereto, something like a shaver blade

was inserted. Thereby, the porous layer was broken, and the wafer was separated into two sheets with the porous Si exposed.

[0175]

The porous Si layer was etched selectively in a mixture of buffered hydrofluoric acid and aqueous 30% hydrogen peroxide (1:5) with agitation. Thereby the porous Si was etched and removed completely with the monocrystalline Si remaining unetched as an etch-stopping material.

[0176]

The etching rate of the nonporous monocrystalline Si was extremely low, the selection ratio of the etching rate of the porous Si being, 10^5 or higher. Therefore, the decrease in thickness of the nonporous layer by etching was practically negligible (several tens of angstrom).

[0177]

Consequently, a monocrystalline Si layer was formed in a thickness of 0.5 μm on a fused quartz substrate. The monocrystalline Si layer did not change at all by the selective etching of the porous Si layer.

[0178]

The cross-section of the Si layer was observed by transmission electron microscopy, and it was confirmed that no additional crystal defect was formed in the Si layer and the excellent crystallinity was

retained.

[0179]

The same results were obtained without forming the oxidation film on the face of the epitaxial Si.

[0180]

The first monocrystalline Si substrate was used repeatedly for the same use after removal of the remaining porous Si and mirror-polishing of the surface.

[0181]

(Example 10)

A first monocrystalline (100) Si substrate of a P-type or N-type having a ground face on both sides and having a diameter of 6 inches, a thickness of 625 μm , and a specific resistance of 0.01 $\Omega\cdot\text{cm}$ was anodized on both faces in a HF solution.

[0182]

The anodization conditions were as shown below.

[0183]

Current density:	5 ($\text{mA}\cdot\text{cm}^{-2}$)
Anodization solution:	$\text{HF}:\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 1:1:1$
Time:	12 \times 2 (minutes)
Thickness of porous Si:	10 (μm) respectively
Porosity:	15 (%)

This substrate was oxidized at 400°C in an oxygen atmosphere for one hour. By this oxidation, the inner wall of the pores of the porous Si was covered

with a thermal oxidation film. On the porous Si formed on the both faces of the substrate, monocrystalline Si was allowed to grow epitaxially in a thickness of 1 μm by CVD (chemical vapor deposition) under the conditions below.

[0184]

Source gas: $\text{SiH}_2\text{Cl}_2/\text{H}_2$
Gas flow rate: 0.5/180 ℓ/min
Gas pressure: 80 Torr
Temperature: 950°C
Growth rate: 0.3 $\mu\text{m}/\text{min}$

The surfaces of the formed epitaxial Si layers were thermally oxidized to form SiO_2 layers in a thickness of 100 nm.

[0185]

A surface of a separately prepared second Si substrate having a 500-nm thick SiO_2 layer was brought into contact in superposition with each of the faces of the above formed two SiO_2 layers respectively, and the contacted matter was heat-treated at 600°C for 2 hours for bonding.

[0186]

The porous layers were bared at the edge face of the wafer, and a liquid such as water was allowed to penetrate into the porous Si. The entire bonded wafer was heated or cooled, whereby the porous Si layers were broken owing to expansion or other causes to allow the

wafer to separate into three sheets with the porous Si exposed.

[0187]

The porous Si layers were etched selectively with a mixture of 49% hydrofluoric acid with aqueous 30% hydrogen peroxide (1:5) with agitation. Thereby the porous Si was etched selectively and removed completely with the monocrystalline Si remaining unetched as an etch-stopping material.

[0188]

The etching rate of the nonporous monocrystalline Si was extremely low, the selection ratio of the etching rate of the porous Si being 10^5 or higher. Therefore, the decrease in thickness of the nonporous layer by etching was practically negligible (several tens of angstrom).

[0189]

Consequently, a monocrystalline Si layer was formed in a thickness of 1 μm respectively on each of the two Si oxidation films simultaneously. The monocrystalline Si layers did not change at all by the selective etching of the porous Si layer.

[0190]

The cross-section of the Si layer was observed by transmission electron microscopy, and it was confirmed that no additional crystal defect was formed in the Si layer and the excellent crystallinity was

retained.

[0191]

The same results were obtained without formation of the oxidation film on the face of the epitaxial Si layer.

[0192]

The first monocrystalline Si substrate was used repeatedly for the same use after removal of the remaining porous Si and flattening of the surface by hydrogen treatment.

[0193]

(Example 11)

A first monocrystalline (100) Si substrate of a P-type or N-type having a diameter of 5 inches, a thickness of 625 μm , and a specific resistance of 0.01 $\Omega\cdot\text{cm}$ was anodized in a HF solution.

[0194]

The anodization conditions were as shown below.

[0195]

Current density:	7 ($\text{mA}\cdot\text{cm}^{-2}$)
Anodization solution:	HF:H ₂ O:C ₂ H ₅ OH = 1:1:1
Time:	4 (minutes)
Thickness of porous Si:	3 (μm)
Porosity:	15 (%)

Subsequently,

Current density:	30 ($\text{mA}\cdot\text{cm}^{-2}$)
Anodization solution:	HF:H ₂ O:C ₂ H ₅ OH = 1:3:2

Time: 3 (minutes)

Thickness of porous Si: 10 (μm)

Porosity: 45 (%)

This substrate was oxidized at 400°C in an oxygen atmosphere for one hour. Thereby the inner wall of the pores of the porous Si was covered with a thermal oxidation film. On the porous Si formed on the substrate, monocrystalline Si was allowed to grow epitaxially in a thickness of 0.3 μm by CVD under the growth conditions below:

[0196]

Source gas: SiH_4

Carrier gas: H_2

Temperature: 850°C

Pressure: 1×10^{-2} Torr

Growth rate: 3.3 nm/sec

The surface of the formed epitaxial Si layer was thermally oxidized to form a SiO_2 layer in a thickness of 100 nm.

[0197]

A face of a separately prepared Si substrate having a 500-nm thick SiO_2 layer was brought into contact in superposition with the face of the above formed SiO_2 layer, and the contacted matter was heat-treated at 700°C for 2 hours for bonding.

[0198]

A force was applied to the first (or second)

substrate in a direction parallel to the second (or first) substrate, whereby the porous Si layer was broken by the shear stress to allow the wafer to separate into two sheets with the porous Si exposed.

[0199]

Then the porous Si layer was etched selectively with a $\text{HF}/\text{HNO}_3/\text{CH}_3\text{COOH}$ type etching solution. Thereby the porous Si was etched selectively and removed completely.

[0200]

The etching rate of the nonporous monocrystalline Si was extremely low, so that the decrease in thickness of the nonporous layer by etching was practically negligible.

[0201]

Consequently, a monocrystalline Si layer was formed in a thickness of 1 μm on the Si oxidation film. The monocrystalline Si layer did not change at all by the selective etching of the porous Si.

[0202]

The cross-section of the Si layer was observed by transmission electron microscopy, and it was confirmed that no additional crystal defect was formed in the Si layer and the excellent crystallinity was retained.

[0203]

The same results were obtained without forming

the oxidation film on the surface of the epitaxial Si layer surface.

[0204]

The first monocrystalline Si substrate was used repeatedly for the same use after removal of the remaining porous Si.

[0205]

(Example 12)

A first monocrystalline (100) Si substrate of a P-type or N-type having a diameter of 5 inches, a thickness of 625 μm , and a specific resistance of 0.01 $\Omega\cdot\text{cm}$ was anodized in a HF solution.

[0206]

The anodization conditions were as shown below.

[0207]

Current density:	7 ($\text{mA}\cdot\text{cm}^{-2}$)
Anodization solution:	HF:H ₂ O:C ₂ H ₅ OH = 1:1:1
Time:	4 (minutes)
Thickness of porous Si:	3 (μm)
Porosity:	15 (%)

Subsequently,

Current density:	30 ($\text{mA}\cdot\text{cm}^{-2}$)
Anodization solution:	HF:H ₂ O:C ₂ H ₅ OH = 1:3:2
Time:	3 (minutes)
Thickness of porous Si:	10 (μm)
Porosity:	45 (%)

This substrate was oxidized at 400°C in an

oxygen atmosphere for one hour. By this oxidation, the inner wall of the pores of the porous Si was covered with a thermal oxidation film. On the porous Si, monocrystalline Si was allowed to grow epitaxially in a thickness of 0.3 μm by CVD under the growth conditions below.

[0208]

Source gas: SiH_4
Carrier gas: H_2
Temperature: 850°C
Pressure: 1×10^{-2} Torr
Growth rate: 3.3 nm/sec

The surface of the formed epitaxial Si layer was thermally oxidized to form a SiO_2 layer in a thickness of 100 nm.

[0209]

A face of a separately prepared Si substrate having a 500-nm thick SiO_2 layer was brought into contact in superposition with the face of the above formed SiO_2 layer, and the contacted matter was heat-treated at 700°C for 2 hours for bonding.

[0210]

The porous layers were bared at the edge face of the wafer, and the porous Si was etched from the edge face with a selective etching solution, whereby the wafer came to be separated into two sheets.

[0211]

Further, the porous Si layer was etched selectively with a $\text{HF}/\text{HNO}_3/\text{CH}_3\text{COOH}$ type etching solution. Thereby, the porous Si was etched selectively and removed completely.

[0212]

The etching rate of the nonporous monocrystalline Si was extremely low, so that the decrease in thickness of the nonporous layer by etching was practically negligible.

[0213]

Consequently, a monocrystalline Si layer was formed in a thickness of $1\text{ }\mu\text{m}$ on the Si oxidation film. The monocrystalline Si layers did not change at all by the selective etching of the porous Si.

[0214]

The cross-section of the Si layer was observed by transmission electron microscopy, and it was confirmed that no additional crystal defect was formed in the Si layer and the excellent crystallinity was retained.

[0215]

The same results were obtained without forming the oxidation film on the surface of the epitaxial Si layer surface.

[0216]

The first monocrystalline Si substrate was used repeatedly for the same use after removal of the

remaining porous Si.

[0217]

[Effects of Invention]

As described in detail, according to the present invention, the first Si substrate can be removed over a large area at the porous layer. The separated first substrate can be reused as the first Si substrate after the remaining porous layer is removed, and after the surface is treated for surface-flattening treatment if the surface flatness is insufficient. The first Si substrate can be reused repeatedly so far as it has necessary strength for the use.

[0218]

The mechanical strength of porous silicon is much lower than that of bulk silicon depending on the porosity thereof. For instance, porous silicon having a porosity of 50% is considered to have half the mechanical strength of bulk silicon. Therefore, on application of a compressive force, a pulling force, or a shearing force to a lamination-bonded wafer, the porous layer will be broken first. The larger the porosity of the porous layer is, the less the force for the breakdown of the layer is.

[0219]

In production of a bonded substrate by a prior art technique, the portions of the first Si substrate

are successively removed from one face by grinding or etching, so that both of the faces of the substrate can not be used effectively for a bonding of the supporting substrate. However, according to the present invention, the first substrate is kept unchanged except the surface layer. Therefore, two bonded substrates can be produced simultaneously by use of one first Si substrate by bonding a supporting substrate to each of both main faces of the first Si substrate. Naturally in this case also, the first Si substrate can be reused as the first Si substrate after removal of the remaining porous layers and grinding of the surfaces.

[0220]

Further, according to the process for producing a semiconductor substrate of the present invention, a monocrystalline Si or a monocrystalline compound semiconductor having excellent crystallinity and uniform flatness over the large area can be produced by selective etching of remarkable selectivity.

[0221]

Furthermore, in the present invention, the porous Si layer can be removed by selective grinding by utilizing the monocrystalline layer as the grinding-stopper owing to the low mechanical strength and large surface area of the porous Si.

[0222]

The present invention can provide a process for producing a semiconductor substrate comprised of preparing a monocrystalline substrate which is economically excellent and uniformly flat over a large area and has an exceedingly excellent crystallinity, and removing a portion thereof from one face of the substrate reaching to an active compound semiconductor layer while leaving a semiconductor layer or the active compound semiconductor layer formed on a surface thereof to obtain the semiconductor layer or the active compound semiconductor layer with few defects on an insulative material.

[0223]

Further, the present invention proposes a process for producing a semiconductor substrate in which a monocrystalline Si or compound semiconductor layer having crystallinity as high as that of a monocrystalline wafer is formed on a transparent substrate (light-transmissive substrate) with high productivity, high uniformity, high controllability, and low production cost.

[0224]

Further, the present invention proposes a process for producing a semiconductor substrate capable of substituting expensive SOS and SIMOX in production of a large scale integrated circuits of an SOI

structure.

[0225]

In the present invention, a monocrystalline compound semiconductor layer can be formed with high crystallinity on porous Si, and this semiconductor layer can be transferred onto an insulative substrate of a large area at low cost. Thereby, a compound semiconductor layer can be formed with high crystallinity on an insulative substrate with sufficient control of the differences in the lattice constants and in the thermal expansion coefficients which are the problems mentioned above.

[Brief Description of the drawings]

[Fig. 1]

A schematic drawing for explaining the process of Embodiment 1 of the present invention.

[Fig. 2]

A schematic drawing for explaining the process of Embodiment 2 of the present invention.

[Fig. 3]

A schematic drawing for explaining the process of Embodiment 3 of the present invention.

[Fig. 4]

A schematic drawing for explaining the process of Embodiment 4 of the present invention.

[Fig. 5]

A schematic drawing for explaining the process of Embodiment 5 of the present invention.

[Explanation of Symbols]

- 11 semiconductor substrate
- 12 Porous semiconductor
- 13 Polycrystalline Si layer
- 14 Si supporting substrate
- 15 Insulative layer
- 21 Semiconductor substrate
- 22 Porous semiconductor
- 23 Polycrystalline Si layer
- 24 Light-transmissive supporting substrate
- 25 Insulative layer
- 31 Semiconductor substrate
- 32 Porous semiconductor
- 33 Polycrystalline compound semiconductor layer
- 34 Si supporting substrate
- 35 Insulative layer
- 41 Semiconductor substrate
- 42 Porous semiconductor
- 43 Monocrystalline compound semiconductor layer
- 44 Light-transmissive supporting substrate
- 45 Insulative layer
- 51 Semiconductor substrate
- 52, 53 Porous semiconductor
- 54, 55 Monocrystalline semiconductor layer
- 56, 57 Supporting substrate

58, 59 Insulative layer

[Document name] Drawings

[Document Name] Abstract

[Summary]

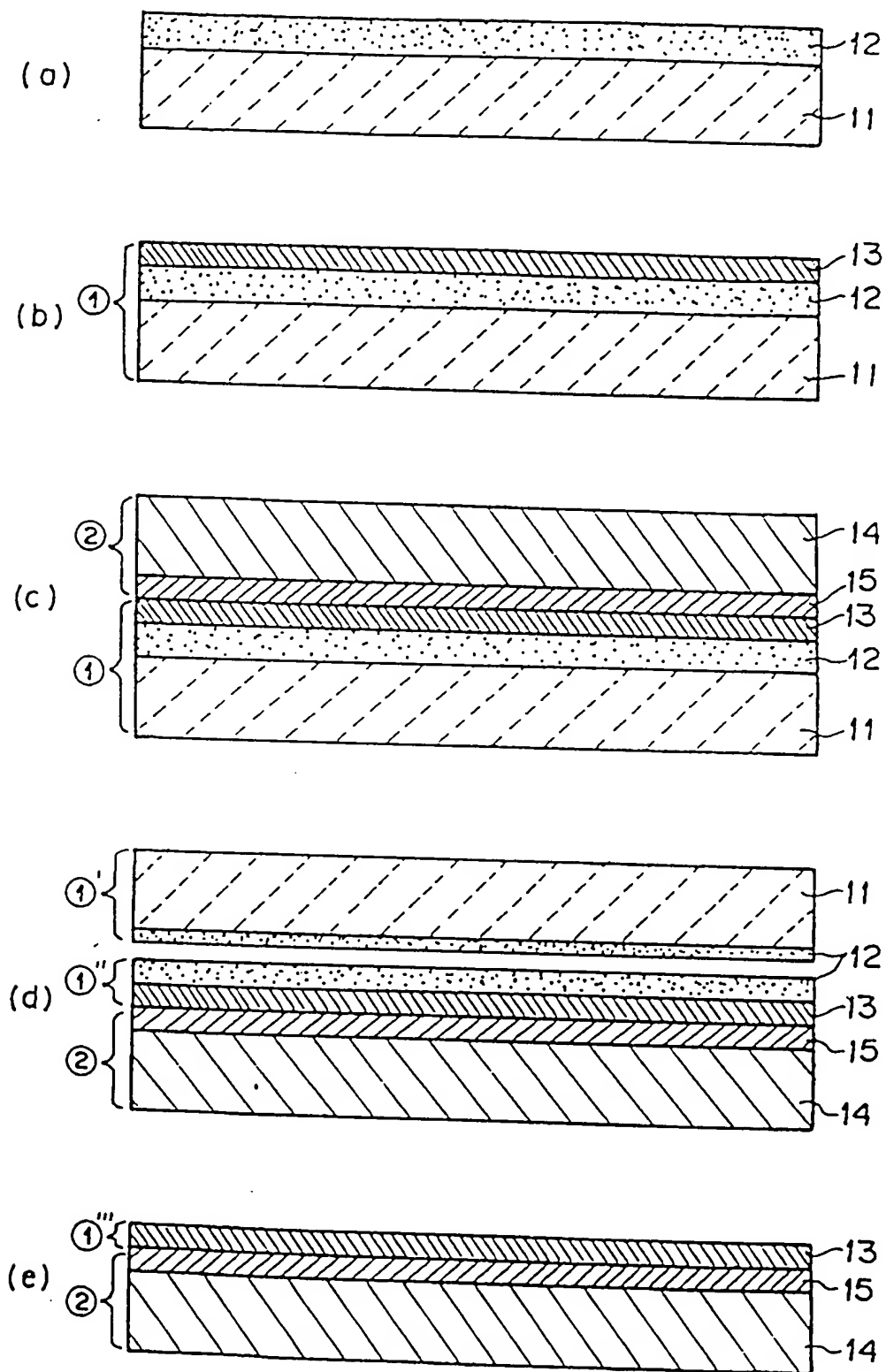
[Objects] The present invention provides a process for producing a semiconductor substrate having a monocrystalline layer of Si or a compound semiconductor monocrystalline layer having crystallinity comparable with monocrystalline wafer on an insulative substrate such as a light-transmissive substrate with excellencies in productivity, uniformity, controllability, and cost.

[Constitution] A process for producing a semiconductor substrate, which comprises steps of (a) making porous (12) a surface layer of at least of a main face side of a first Si substrate 11, (b) forming a monocrystalline semiconductor layer 13 on the porous Si layer 12, (c) bonding the monocrystalline layer 13 onto a main face of a separately prepared supporting substrate 14 with or without interposition of an insulative layer 15, (d) separating the bonded substrates at the porous layer, (e) and removing selectively only the porous Si layer 12 exposed on the supporting substrate.

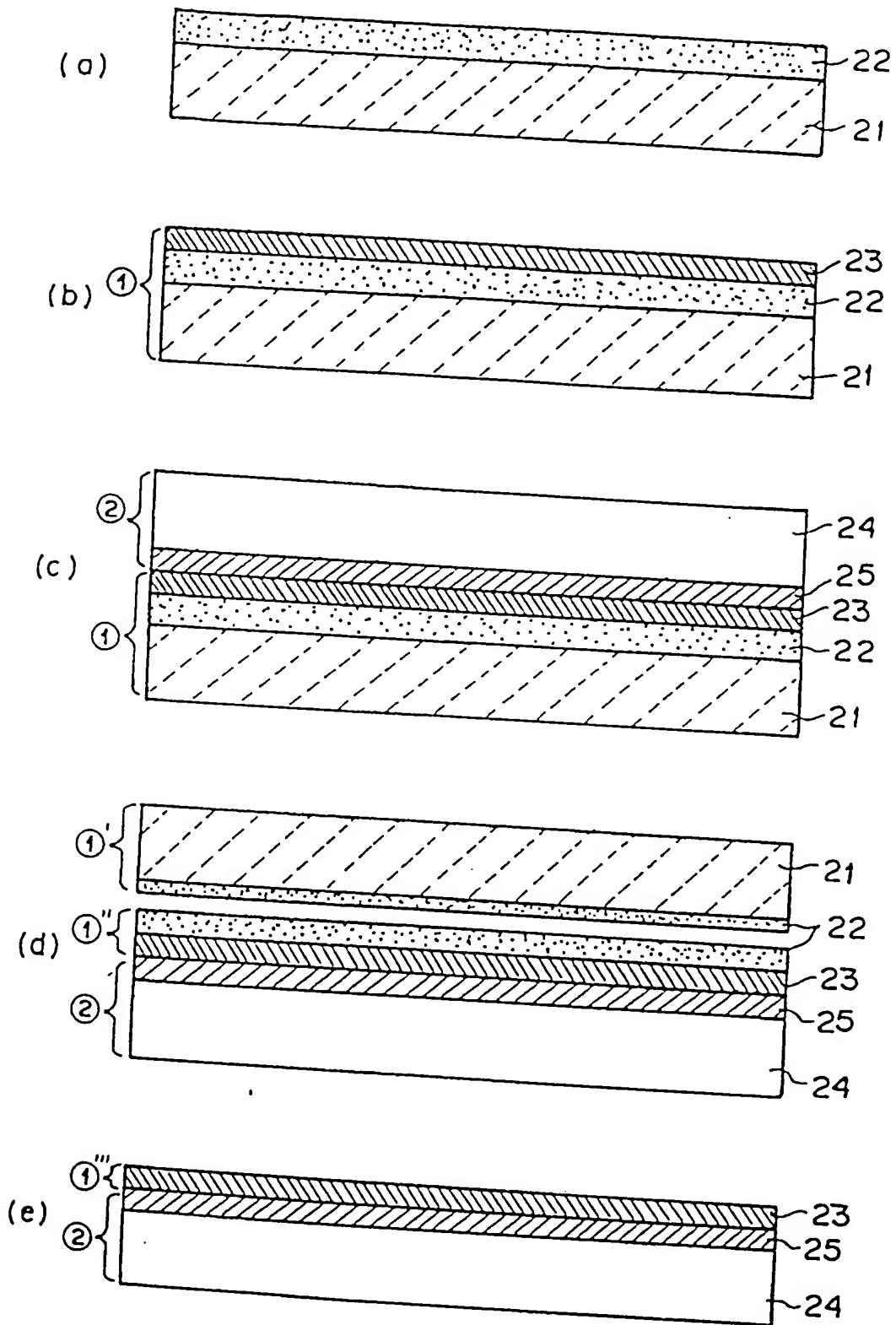
[Selected Drawing] Fig. 1

【書類名】 図面

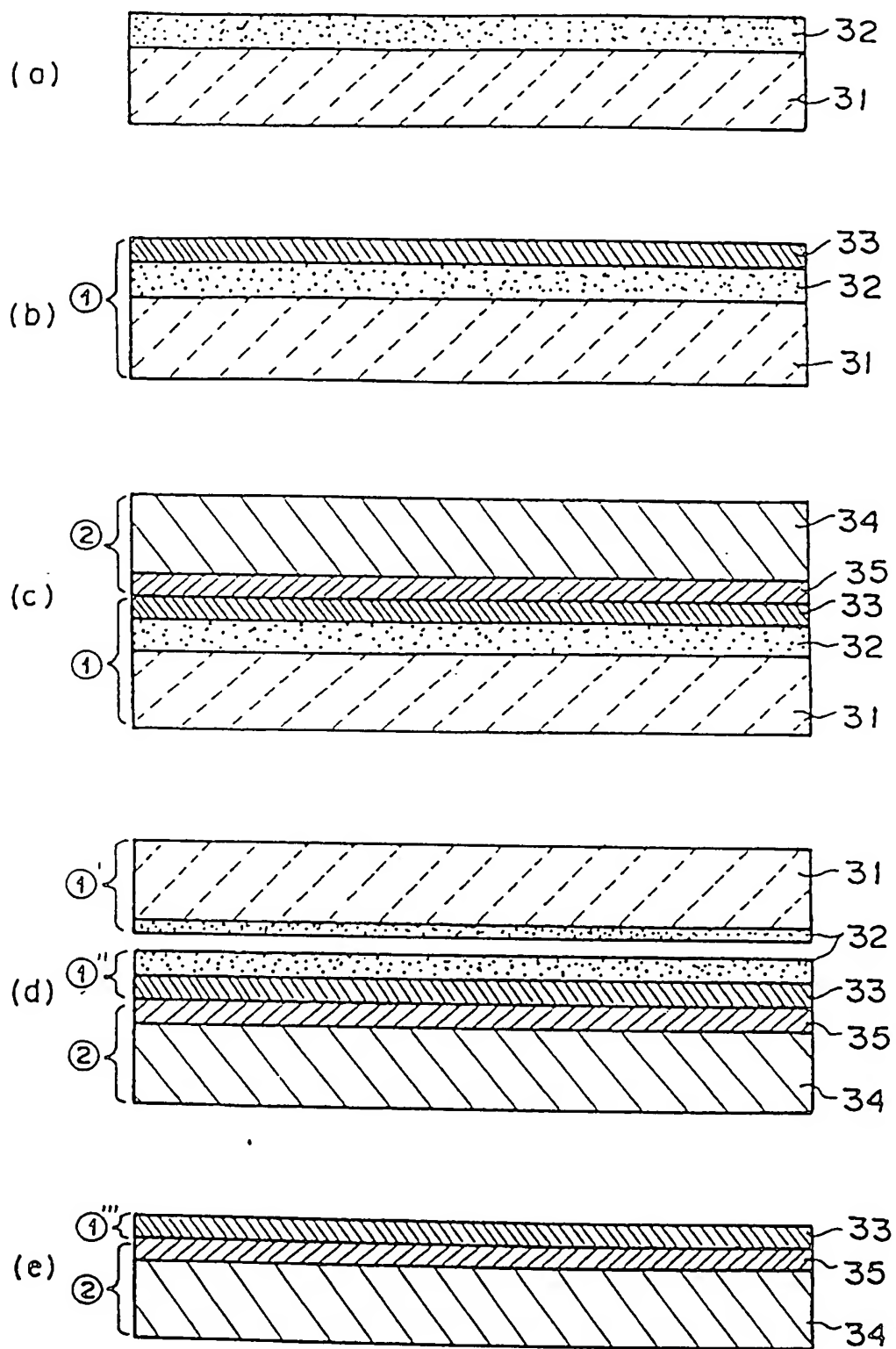
【図 1】 *Fig. 1*



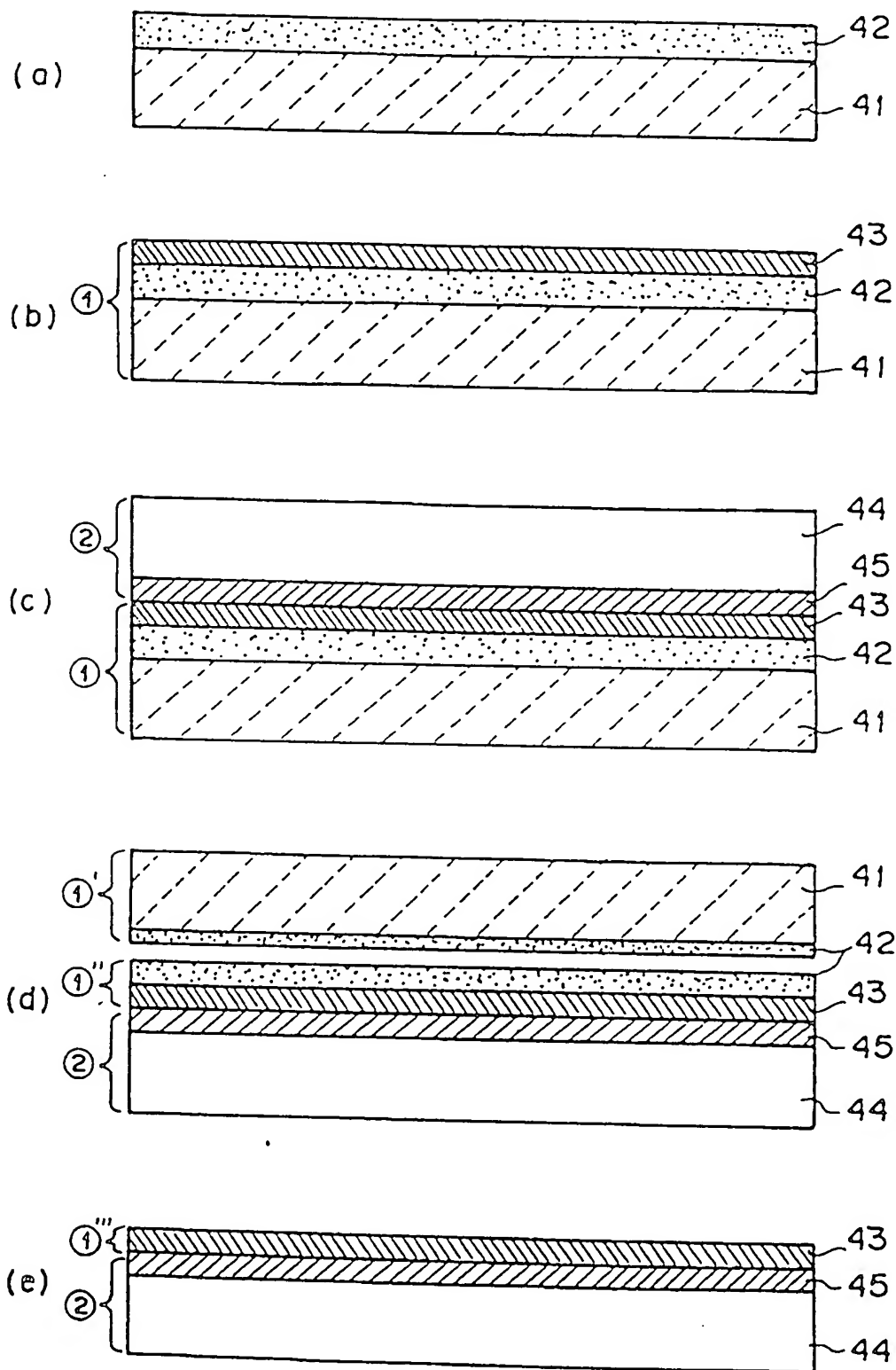
【図2】 Fig. 2.



【図 3】 Fig. 3.



【図 4】 Fig. 4



【図5】 Fig. 5.

